Effects of polydispersity on the phase coexistence diagrams in multiblock copolymers with Laser block length distribution

M. Foroutan[a,c*] and M. A. Jafarizadeh[b,c,d†].

[a]Department of Physical Chemistry, Faculty of Chemistry, Tabriz University, Tabriz 51664, Iran.

[b]Department of Theoretical Physics and Astrophysics, Tabriz University, Tabriz 51664, Iran.

[c]Institute for Studies in Theoretical Physics and Mathematics, Teheran 19395-1795, Iran.

[d]Research Institute for Fundamental Sciences, Tabriz 51664, Iran.

February 1, 2008

---

[*]E-mail:m.foroutan@tabrizu.ac.ir

[†]E-mail:jafarizadeh@tabrizu.ac.ir

Abstract

Phase behavior of **AB**-multiblock copolymer melts which consists of chains with Laser distribution of **A** and **B** blocks have been investigated in the framework of the mean-field theory, where the polydispersity of copolymer is a function of two parameters **K** and **M**. The influence of the Laser distribution on higher order correlation functions (up to sixth order) are computed for various values of **K** and **M**, and their contributions on the phase diagrams and phase coexistence are presented. It is shown that, with increasing polydispersity (decreasing **K** and increasing **M**) the transition lines of all phases shift upwards, consequently polydispersity destabilize the system.

Keywords:phase coexistence, Laser distribution, polydispersity, block length, Phase diagram, multiblock copolymer melts, correlation functions .

PACs numbers:05.45.Ra, 05.45.Jn, 05.45.Tp

I   Introduction

Recently several publications have been appeared in connection with block copolymer systems from both theoretical [1, 2, 3] and experimental [4, 5, 6] aspects. In **AB** multiblock copolymer melts, the immiscibility between **A** and **B** blocks induces self-assembly into various ordered microstructures. With decreasing the temperature, multiblock copolymers with repulsive interaction between different monomers undergo a microphase separation transition manifesting an energetic preference for contacts between similar monomers. In this work , the system will be studied in the weak segregation regime, where the separation between the **A** and **B** monomers is not complete. The theoretical investigations demonstrate that it is very possible that these (microphases separated) single phase are metastable and the free energy can be lowered even more by splitting the system into coexistence phase [7]. The properties of copolymer depend not only on the nature of the comonomers and the overall compositions, but also on the distribution of monomer units along the chain. As an example one can consider N-vinyl pyrrolidone (VP) and vinyl acetate (VA) copolymer. This copolymer can be synthesized in different ways resulting in the different homogeneity of backbone monomer distribution. Experimental studies show that the monomer unit distribution has effect on solution properties,particularly when the mole ratio VP to VA in the copolymer is close to unity, sequence distribution plays an important role in solution behavior [8]. In this work as in Reference [9], we use the most comprehensive distribution, namely Laser distribution with two parameters **K** and **M** as the controller of degree of polydispersity. Polydispersity is an important parameter which can effect many physical properties of a polymer. Recently in an experimental work, the polydispersity lower than 1.0 is reported [10]. Also the theoretical models with polydispersity values of lower than unity can be useful for molecular weight distributions based on complex numbers [11].

The aim of the present paper is to investigate the effect of the parameters of the Laser distribution on the position of the phase transition lines, the stability of the various microstructre

and the position of the phase coexistence in multiblock copolymer.

We consider an incompressible multiblock copolymer melt in which both the lengths of **A**-blocks and **B**-blocks satisfy Laser distribution. The phase behavior of the multiblock copolymer melt is calculated in the mean-field theory. By using this theory it is shown that there are regions in the phase diagrams where two phases with different symmetry of the superlattice (lamellar, hexagonal and bcc) coexist with each other in the finite temperature range. Since the block lengths in the system are assumed very large, this approximation becomes more accurate and we can ignore the fluctuation corrections [12].

The paper is organized as follows: In section **II**, the model and the block length distribution are explained in details. Using the block length distribution one can calculate the correlation functions which are required for determination of the vertex functions of Landau free energy of multiblock copolymer. In section **III** we calculate the higher correlation functions up to sixth order and then the effects of the Laser distribution and Schultz distribution on them are compared. In section **IV** we give a general expression for the Landau free energy of a broad class of polydisperse multiblock copolymers. In Section **V** the influence of the parameters **M** and **K** on phase diagrams of **AB** multiblock copolymers are discussed. The paper ends with conclusion and two appendices.

II   Laser distribution and its polydispersity

We consider an incompressible multiblock copolymer melts consisting of two types of blocks **A** and **B** in which length of both **A** and B blocks obeys Laser distribution. Generally the block length distribution is the statistical representation of the probability of attachment of one block to another block. The Laser distribution is used for the first time as a comprehensive block length distribution in multiblock copolymers in Reference[9], such that it can be reduced to other distributions in special cases. The normalized Laser distribution is defined

as [13]:

$$P(n) = \frac{K(M+1)^{\frac{K+1}{2}}}{n_n M}(\frac{n}{n_n})^{\frac{K-1}{2}} \exp(\frac{-K}{M} - \frac{Kn(M+1)}{n_n M})I_{K-1}(\frac{2Kn^{\frac{1}{2}}(M+1)^{\frac{1}{2}}}{n_n^{\frac{1}{2}} M}),$$

where $K > 0$ and I_{k-1} is modified Bessel function. For $K = 1$, the Laser distribution reduces to the Laguerre distribution. As $M \longrightarrow \infty$, the Laser distribution reduces to Schultz-Zimm distribution[14, 15]. Finally for $K = 1$ and in the limit of $M \longrightarrow \infty$, the Laser distribution reduces to the Flory distribution. As it will be shown in Appendix **I**, the polydispersity of the Laser distribution is equal to $\frac{M(M+2)}{K(M+1)^2}$. Clearly as **M** becomes infinite, its polydispersity reduces to $\frac{1}{K}$.

III   Higher correlation functions

In this section, we calculate the higher correlation functions, that is, the fourth, the fifth and the sixth order correlation functions. The calculation of the lower correlation function are given in details in Appendix II. The higher order correlation functions are defined as:

$$g_{AAAA} = 4!(n_A + n_B)^3(-\frac{3(1-\alpha)}{y^4} + \frac{f - 2\alpha'}{y^3} + \frac{\alpha''}{2y^2})$$

$$g_{AAAAA} = 5!(n_A + n_B)^4(\frac{4(\alpha - 1)}{y^5} + \frac{f - 3\alpha'}{y^4} + \frac{\alpha''}{y^3} - \frac{\alpha'''}{6y^2})$$

$$g_{AAAAAA} = 6!(n_A + n_B)^5(\frac{3(\alpha - 1)}{y^6} - \frac{f + 4\alpha'}{y^5} + \frac{3\alpha''}{2y^4} - \frac{\alpha'''}{3y^3} + \frac{\alpha''''}{24y^2})$$

with

$$\alpha^{(i)} = (\frac{-1}{n_A + n_B})^i \int dn n^i \exp(-nx)P(n)$$

where $\alpha^{(i)}$ corresponds to $\alpha, \alpha', \alpha'', \alpha''', \alpha''''$ for i=0,1,2,3,4, respectively . As it is shown in the above equation, the value of $\alpha^{(i)}$ depends on the distribution function P(n) where here we use the most comprehensive distribution, that is, Laser distribution, where it can be reduced to Schultz distribution for paticular values of its parameters. In order to obtain the correlation

functions, we have to calculate the Laplace transforms of $\alpha(y)$. The Laplace transforms of $\alpha(y)$ (corresponding to Laser distribution) are:

$$\alpha^{(i)} = R! i! \beta^{k-1} \gamma^{-(k+i)} L_i^{(k-1)} (-\frac{\beta 2}{\gamma})$$

$$R = \frac{k(M+1)^{\frac{k+1}{2}}}{Mn_n} (\frac{1}{n_n})^{\frac{k-1}{2}} \exp{(\frac{-k}{M})}$$

$$\gamma = \frac{k(M+1) + Mn_n}{Mn_n}$$

and

$$\beta = \frac{k(M+1)}{Mn_n^{\frac{1}{2}}},$$

where the expression $L_i^{(k-1)}$ is the Laguerre function. The influence of the parameters **K** and **M** on the shape of the second, the third and the sixth order correlation functions are given in the figures 1a to 1c. The form of the third, fourth, fifth and sixth order correlations are same but their scales are very different(they are of order: 10^9, 10^{15}, 10^{21} and 10^{27}, respectively). If we apply the Schultz distribution, we obtain only the first point of the right hand of the curves. It should be reminded that as $M \longrightarrow \infty$, the Laser distribution reduces to Schultz-Zimm distribution.

IV   Theory of Landau free energy

From the point of view of Landau's phase transition theory [16], a system under microphase separation undergoes a set of phase transitions which are described in terms of the order parameter:

$$\psi(x) = \rho_A(x) - < \rho_A >,$$

where $\rho_A(x)$ is the local density of **A** monomers and $< \rho_A >$ is the average value of the density over the volume **V** of the system. At low temperature, the order parameter can

become a spatially periodic function, which possesses the symmetries of a certain space group ζ i.e. :

$$\psi(\vec{q}) = \Sigma_{\vec{Q}\in\hat{L}}A_{\vec{Q}}\exp{(i\Phi_{\vec{Q}})}\delta(\vec{q}-\vec{Q}),$$

where $\psi(\vec{q})$ is the Fourier transform of concentration profile $\psi(x)$, $\hat{L}$ is the reciprocal of the lattice L describing the translational symmetries of ζ, the amplitudes A_Q and phases Φ_Q are adjustable parameters. The free energy of the system is :

$$F(\chi, f) = -K_BT\ln Z(\chi, f),$$

where T is temperature, K_B is Boltzmann's constant, χ is the Flory-Huggins parameter, **f** is volume fraction of the A block and Z is the partition function defined as the integral over all possible profiles $\psi(x)$, i.e. :

$$Z = \int d\psi \exp{(-H(\psi(x))/K_BT)},$$

where the effective Hamiltonian, $H(\psi(x))$ is the virtual free energy of the state with a given $\psi(x)$. Since we assume that $\rho_A(x)$ differs from $<\rho_A>$ only slightly, the free energy for each symmetries of the superlattice i may be approximated by its Landau's expansion in powers of $\psi(x)$, i.e. :

$$F_L^i(\psi(x)) = K_BT\sum\frac{1}{n!}\int dx_1\cdots dx_n\Gamma_n(x_1\cdots x_n)\psi(x_1)\cdots\psi(x_n),$$

with vertices Γ_n defined as :

$$\Gamma_2(\overrightarrow{q_1}, \overrightarrow{q_2}) = V\delta_k(\overrightarrow{q_1}, \overrightarrow{q_2})[\frac{g_{AA}(q_1) + 2g_{AB}(q_1) + g_{BB}(q_1)}{g_{AA}(q_1)*g_{BB}(q_1) - g_{AB}^2(q_1)} - 2\chi],$$

$$\Gamma_3(\overrightarrow{q_1}, \overrightarrow{q_2}, \overrightarrow{q_3}) = -V\delta_k(\overrightarrow{q_1}, \overrightarrow{q_2}, \overrightarrow{q_3})\sum g_{\alpha\beta\gamma}(\overrightarrow{q_1}, \overrightarrow{q_2}, \overrightarrow{q_3})z_\alpha(q_1)z_\beta(q_2)z_\gamma(q_3),$$

where $g_{\alpha\beta}$ and $g_{\alpha\beta\gamma}$ are second and third correlation functions, respectively, and

$$z_\alpha(q) = g_{\alpha A}^{-1}(q) - g_{\alpha B}^{-1}(q).$$

After inserting the trial function $\psi(x)$ in Landau free energy, the lowest order term F_2 attains the form:

$$\frac{F_2}{V} = \gamma_2 A^2,$$

This expression is independent of the structure. The third order and fourth order contribution to free energy are different for the various structures:

$$\frac{F_3^{hex}}{V} = -\frac{2 \mid \gamma_3 \mid A^3}{3\sqrt{3}},$$
$$\frac{F_3^{bcc}}{V} = \frac{-4 \mid \gamma_3 \mid A^3}{3\sqrt{6}},$$
$$\frac{F_3^{lam}}{V} = 0,$$

while the fourth order contribution to the free energy has the form

$$\frac{1}{4!} \sum_{\vec{q_1}, \vec{q_2}, \vec{q_3}, \vec{q_4}} \Gamma_4(\vec{q_1}, \vec{q_2}, \vec{q_3}, \vec{q_4}) A^4.$$

In order to obtain the vertices of multiblock copolymer whose blocks lengths obey a certain distribution $\mathbf{P(n)}$, we have to calculate the correlation functions. The general expressions for the correlation functions are investigated in Appendix II. The phase diagram can be obtained by numerical minimization of free energy with respect to the parameters $\mathbf{A}$ and $\mathbf{y}$. Several phases with different superlattice structure can coexist with each other. Considering a two-phase state with the volume fractions $\mathbf{x}$ and $(\mathbf{1 - x})$ occupied by phases 1 and 2, respectively, the final expression for the free energy can be defined as :

$$F = xF_1(A_1, y_1) + (1 - x)F_2(A_2, y_2) - \frac{1}{2}x(1 - x)J$$

and

$$J = 4(\frac{1}{y_1} + 1)A_1^4 + 8(\frac{1}{y_1 + y_2} + 1)A_1^2 A_2^2 - 4(\frac{1}{y_2} + 1)A_2^4.$$

Here the phase diagram can be obtained by numerical minimization of free energy with respect to the parameters $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{y_1}$ and $\mathbf{y_2}$ and $\mathbf{x}$ for each coexistence.

V   The influence of the polydispersity on the phase diagrams and phase coexistence

In this section phase coexistence for various values of polydispersity with Laser distribution are presented in the framework of the mean-field theory. Here diagrams in the immediate vicinity of the critical point of the multiblock copolymers for $\mathbf{K} = \mathbf{1}$ to 40 and $\mathbf{M} = \mathbf{0.01}$ to 100 are constructed. Figure 2 shows the mean-field phase diagrams for the most polydispers and the most monodisperse systems, respectively. In figure 2a, $\mathbf{M}$ is very large and $\mathbf{K}$ is very small and in figure 2b, $\mathbf{M}$ is very small and $\mathbf{K}$ is very large. Figures 3 and 4 show the mean-field phase diagram for the multiblock copolymer melts in terms of variables $\mathbf{N}\chi$, where χ is the interaction parameter and $\mathbf{f}$ is the monomer fraction. In these figures system is at very high polydisperse and very low polydiperse states , respectively . It should be reminded that according to the equation of the polydispersity of Laser distribution, the polydispersity increases with increasing of $\mathbf{M}$ and decreasing of $\mathbf{K}$. These figures show that the region of the stability of the phase coexistence shift considerably to the larger $\mathbf{N}\chi$ with increasing polydispersity. Figures 5 and 6 show the one-dimensional phase diagrams of multiblock copolymer with $\mathbf{f} = \mathbf{0.25}$ for $\mathbf{K} = \mathbf{1}$ and $\mathbf{K} = \mathbf{40}$, respectively. One can see that for low values of $\mathbf{K}$, the value of $\mathbf{M}$ has not considerable effect on the stability region of microphases while its effect is very large for higher values of $\mathbf{K}$. Therefore, for large values of $\mathbf{K}$, with the decreasing of $\mathbf{M}$, the transition lines of the phases shifts severely upwards, while for small values of $\mathbf{K}$ these changes are very slow. Great attention should be paid to the scales in this figure. Even though these scales are unphysical, but it can be very useful

in showing the sensitivity of $\mathbf{N}\chi$ to M. The dependence of the $\mathbf{N}\chi$ on polydispersity, in the high polydisperse and low polydisperse systems, with $\mathbf{f} = \mathbf{0.25}$, are given in figures 7 and 8, respectively. These figures show that for small values of $\mathbf{K}$ with increasing of $\mathbf{M}$ the slope of the curve is slow, while for large values of $\mathbf{K}$, it is very sharp.

CONCLUSION :

In the present paper we have introduced the most comprehensive distribution function for the polydispersity of molecular weight distributions that is the Laser distribution. Laser distribution with two parameters $\mathbf{K}$ and $\mathbf{M}$ can be reduced to other distributions. The Flory distribution and Schultz-Zimm distribution are $\mathbf{M} \longrightarrow \infty$ limiting case of Laser distribution, therefore, so far the role of finite values of $\mathbf{M}$ has not been considered. Actually in this work we see that the effect of $\mathbf{M}$ (especially for the low $\mathbf{M}$) on the curve of distribution versus block length and also its effect on the phase behaviour of multiblock copolymer is very interesting.

Appendix I : The polydispersity of distributions

Here in this appendix we derive the polydispersity of distribution functions. According to section III the polydispersity is defined as :

$$U = \frac{< n^2 > - < n >^2}{< n >^2},$$

where

$$< n^i >= \int dn P(n) n^i.$$

Using the above formulas we calculate the polydispersity of Laser distribution which is comprehensive enough to include the other known distributions as a limiting cases. Hence we can

obtain the polydispersity of other distributions from this one. In calculating polydispersity of Laser distribution we have to use the following integral:

$$\int_0^\infty dx x^{p+v/2} \exp(-\alpha x) I_v(2\beta x^{\frac{1}{2}}) = p! \beta^v \exp\left(\beta^2/\alpha\right) \alpha^{(-p-v-1)} L_v^p(-\beta^2/\alpha)$$

. Using the above integral we obtain the following expression for the p-moment of laser distribution:

$$< x^p >= p! \alpha^{-p} L_p^{k-1}(-\beta^2/\alpha),$$

where

$$L_p^v(x) = (1/p!) x^{-v} \exp(x) (d/dx)^p (x^{v+p} \exp(-x))$$

is the Laguerre polynomial of order p. Now, using the first and second moments we obtain the following expression for polydispersity of Laser distribution:

$$U = \frac{M(M+2)}{K(M+1)^2}.$$

Obviously for $K = 1$ we get the Laguerre distribution with polydispersity $U = 1 - \frac{1}{(M+1)^2}$

and as $\mathbf{M} \to \infty$ we obtain the Schultz-Zimm distribution with polydispersity $U = \frac{1}{K}$ where

Flory distribution with polydispersity $U = 1$ can be obtained from it for $K = 1$.

Appendix II: The Correlation Functions of Multiblock Copolymer [17]

In a polydisperse multiblock copolymer melt several molecule types are presented. if $\mathbf{s}$ denotes a molecule type (i.e. a finite sequence of $\mathbf{A}$-blocks and $\mathbf{B}$-blocks) and if $\rho_{\mathbf{s}}$ denotes the number density of molecules of type s, then the composition of the melt is fixed completely by the set $\rho_{\mathbf{s}}$. A molecule s is fixed if the lengths of all blocks in the molecule are fixed:

$$s = (N_A^1, N_B^1, N_A^2, N_B^2, \ldots, N_A^Q, N_B^Q)$$

where N_α^i denotes the length of the ith block of type α in the molecule. In this work we have assumed that the number of molecule (Q) is very large. Here $P_\alpha(n)$ denotes the probability that a block of type α has a length between n and n+dn. For this distribution we have :

$$\int_0^\infty dn P_\alpha(n) = 1$$

and

$$\int_0^\infty dn P_\alpha(n) = n_\alpha,$$

where n_α is the average length of a block of type α. The quantity ρ_s can be defined as:

$$\rho_s = cP_s = cP_A(N_A^1)P_B(N_B^1)P_A(N_A^2)P_B(N_B^2)\dots P_A(N_A^Q)P_B(N_B^Q).$$

The normalization constant **c** is determined by the constraint that the monomer density is unity, i.e. :

$$\sum_s \rho_s N_s = 1,$$

where N_s is the total molecule length. Combining the above equations gives the normalization constant c:

$$c = \frac{1}{Q(n_A + n_B)}.$$

Now we calculate the second order function. The average second order function over the composition ρ_s is given by:

$$g_{\alpha\beta} = \sum_s \rho_s \sum_{i,j} \sigma_i(\alpha)\sigma_j(\beta) \exp(-q^2 \mid j - i \mid)$$

where $\sigma_i(\alpha)$ equals 1 only if block i is of type α and otherwise is zero. Where i and j are many blocks apart, the weight factor $\exp(-q^2 \mid j - i \mid)$ will give a negligible contribution to the correlation function, and one gets a contribution only if the number of blocks between i and j is of order unity. Here for simplicity, the calculation of the correlation function where i and j are in the same block are given. For second correlation function, the **AA**-component

of the second order correlation function is equal to :

$$g_{AA} = \frac{1}{Q(n_A + n_B)} 2Q \int dn P(n) \int_0^n di \int_0^n dj \exp(-x(j-i)) =$$

$$\frac{2}{n_A + n_B} \int dn P(n) \frac{n}{x} + \frac{\exp(-nx)}{x^2} - \frac{1}{x^2} = (n_A + n_B)(\frac{-2(1-\alpha(y))}{y^2} + \frac{2f}{y})$$

where:

$$f = \frac{n_A}{n_A + n_B} \quad , x = q^2 \quad , y = (n_A + n_B)x, \alpha(y) = \int dn \exp(-nx) P(n)$$

For the **BB**-component of the second order correlation function, $\beta(y)$ is used to as the Laplace transform of the length distribution of the **B**-blocks. Since the states corresponding to $i < j$ give the same contribution as $j < i$ ones, one should take into account a factor 2 due to this symmetry. Finally the factor Q can be interpreted as the number of blocks in which monomer i can be presented. The contribution third order correlation function for the situation where all three monomer are in same block **A** is :

$$g_{AAA} = \frac{1}{Q(n_A + n_B)} 3! Q \int_0^\infty dn P(n) \int_0^n di \int_i^n dj \int_j^n dk \exp(-x(k-i))$$

$$= 6(n_A + n_B)^2 (-\frac{2(1-\alpha)}{y^3} + \frac{f - \acute{\alpha}}{y^2})$$

$\acute{\alpha}$ is the derivative of α with respect to y:

$$\acute{\alpha}(y) = d/dy \int_0^\infty dn \exp(-nx) P(n)$$

$$= -\frac{1}{(n_A + n_B)} \int_0^\infty dn n \exp(-nx) P(n)$$

References

[1] K. BINDER, H. L. FRISCH, *Eur. Phys. J. B.10(1), 71 (1999).*

[2] M. MATSEN, R. B. THOMPSON *j. Chem. Phys., 111(15), 7139 (1999).*

[3] L. KIELHORN, M. MUTHUKUMAR, *j. Chem. Phys., 110(8), 4079 (1999).*

[4] T. RAGER, W. MEYER, G. WEGNER *Macromolecular Chemistry and Physics, 200(7), 1672 (1999).*

[5] H. M. ZHANG, E. RUCKENSTEIN, *Macromolecules, 32(17), 5495 (1999).*

[6] A. B. LOWE, N. C. BILLINGHAM, S. P. ARMES, *Macromolecules, 32(7), 2141 (1999).*

[7] A. NESARIKAR, M. OLVERA DE LA CRUZ, B. CRIST, *j. Phys. Chem., 98, 7385 (1993).*

[8] A. ZHONG, P. WOLF, *J. Appl. Polym. Sci., 74, 345 (1999).*

[9] M. FOROUTAN AND M. A. JAFARIZADEH, *Physica A 307, 221 (2002)*

[10] C. H. ADAMS, L. R. HUTCHINGS, P.G. KLEIN, R. W. RICHARDS, *Macromolecules, 29, 5717 (1996).*

[11] P. EIBECK, *J. Creat. Sci., 1, 6-8 (1999).*

[12] G. H. FREDRICKSON, E. HELFAND *J. Chem. Phys. 87, 697 (1987)*

[13] P. CARRUTHERS, C.C. SHIH, *Int. J. Mod. Phys., A2, 1447 (1987).*

[14] G.V.Z. SCHULTZ, *j. Phys. Chem., Leipzig, B43, 25 (1939).*

[15] B.H. ZIMM, *J. Chem. Phy., 16, 1099 (1948).*

[16] L. D. LANDAU, E. M. LIFSHITZ, *Statistical Physics, part 1, Nauka, Moscow (1976).*

[17] H.J. ANGERMAN, *Ph.D. dissertation, University of Groningen, Netherlands (1998)*

Figures captions

FIG. 1. Dependence of the second, third and sixth order correlation functions on the value of **K** for various values of **M**, respectively (1a-1c).

FIG. 2.Mean-field phase diagrams in the vicinity of the critical point for multiblock copolymers for the most polydispers and the most monodisperse system, respectively. The lower line separates the disordered phase from the bcc phase, the middle line separates the bcc phase from the hexagonal phase and the upper line separates the hexagonal phase from the lamellar phase. $(2a)$ **K** $=$ **1** and **M** $=$ **100**. $(2b)$ **K** $=$ **40** and **M** $=$ **0.01**.

FIG. 3. Mean-field phase diagram in the vicinity of the critical point for multiblock copolymers with **K** $=$ **1** and **M** $=$ **100**. White areas denote single phase regions lam, hex and bcc from up to down, respectively. Black areas denote the regions of coexistence of 2-phases.

FIG. 4. Mean-field phase diagram in the vicinity of the critical point for multiblock copolymers with **K** $=$ **40** and **M** $=$ **0.01**. White areas denote single phase regions lam, hex and bcc from up to down, respectively. Black areas denote the regions of coexistence of 2-phases.

FIG. 5. The one-dimensional phase diagrams of the multiblock copolymer melts **f** $=$ **0.25** for the Laser distribution with **K** $=$ **1** for various values of **M**.

FIG. 6. The one-dimensional phase diagrams of the multiblock copolymer melts **f** $=$ **0.25** for the Laser distribution with **K** $=$ **40** for various values of **M**.

FIG. 7. Dependence of the parameter **N**χ on the polydispersity from $M = 0.01$ to $M \longrightarrow \infty$ for $K = 1$.

FIG. 8. Dependence of the parameter $N\chi$ on the polydispersity from **M** $=$ **0.01** to **M** $\longrightarrow \infty$ for **K** $=$ **40**.